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Synthetic Organic Chemicals

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Furfural Derivatives

THE industrial possibilities of furfural and its derivatives are a problem for the future and a distinct challenge to those who are interested in developing dormant natural resources. At the present time much fundamental work is being done by many of the prominent research laboratories on the utilization of furan compounds. And in the selection of new chemicals for our list a great deal of attention has been paid to the preparation of furfural derivatives in the hope that they will aid in a systematic attack on this problem.

Furfural, up to the year 1922, was in reality a laboratory curiosity, but with the advent of the process now used by the Quaker Oats Company of Cedar Rapids, Iowa, the compound has become the least expensive of all organic aldehydes and can be purchased in large quantities at a low price. Various estimators have placed the possible production of furfural from pentosan-containing agricultural by-products at figures varying from 35,000,000 to 100,000,000 tons each year for the United States.

Furfural diacetate is one of the most useful of the derivatives of furfural for synthetic purposes. This compound has proved to be of great value in the preparation of the 5-nitro, bromo, and chloro derivatives due to the blocking of the aldehyde group. Furfural diacetate can be reduced with palladium oxide and hydrogen to tetrahydrofurfural diacetate which can be hydrolyzed with dilute sulfuric acid to tetrahydrofurfural. There are many as yet unprepared derivatives which can be made from the nitro and halogen derivatives mentioned. The possibility of preparing a sulfofurfural is suggested.

Furoyl chloride is one of the most stable, yet reactive, of the known furan compounds. It is very useful in the preparation of a great variety of aromatic and aliphatic esters and amides, and in other normal reactions of acid chlorides. A number of chlorine- and bromine-substituted furoyl halides can be prepared from the acid chloride and the various halogens. The acid chloride will react with benzene, phenol, and resorcinol in the presence of aluminum chloride to give the various ketones.

Furoamide is a stable compound which can be dehydrated by means of phosphorus pentachloride to the very interesting furonitrile. The acidamide can be transformed to the thioacidamide by the action of phosphorus pentasulfide in benzene.

One of the most interesting of the known furan derivatives is furonitrile which has been shown to be 100 times as sweet as sugar. However, this compound has not been thoroughly tested for its physiological action on animals. The nitrile reacts with hydrogen sulfide to form the thioamide, and with hydrogen chloride and absolute alcohol to form

the imido ether which has valuable synthetic possibilities. Furonitrile reacts with the Grignard reagent to form ketones, and can be reduced to furfurylamine with zinc and sulfuric acid.

Furfuraldoxime is a comparatively stable compound and is a convenient starting point for a number of interesting preparations. Both forms of the oxime have been shown to be 2.5 times as sweet as sugar, which is sharply contrasted with 5-benzyl-2-furfuraldoxime, the syn-isomer of which is 690 while the anti- is 100 times as sweet as sugar. Furfuraldoxime can be reduced to furfurylamine in 40% yields with sodium in absolute alcohol, and with palladium oxide and hydrogen to di-α-furfurylamine. It is quite possible that a catalytic method can be developed to prepare the amine in good yield from the oxime. The amine if produced in quantities should prove to be of value in the preparation of many new and interesting compounds. Methods are described in the literature for preparing furonitrile from the oxime by the action of acetic anhydride.

Furylacrolein is a convenient starting point for a number of interesting syntheses. The aldehyde can be reduced by Adam's platinum oxide catalyst to tetrahydrofuryl-3-propanol-1, from which the chloride is easily prepared by the action of thionyl chloride in good yields. A Grignard reagent can be readily prepared from the chloride in excellent yields. The furyl-3-propanols are also obtained from the aldehyde.

Furylacroleinoxime in contrast to furfuraldoxime, furylacetaldoxime, and 5-benzyl-2-furfuraldoxime, is not sweet. These facts are important to those who are interested in the theoretical aspects of taste and constitution in organic compounds. The oxime can be reduced by means of sodium in absolute alcohol to furylpropylamine, which has synthetic possibilities.

Furylacrylamide is of value because of the preparation of furylacryloylnitrile from it by the action of phosphorus pentachloride. This very interesting nitrile has been shown to be 200 times as sweet as sugar, but its physiological properties are as yet unknown. Thiofurylacrylamide can be prepared from the acidamide by treating it with phosphorus pentasulfide in benzene.

Furfuralacetophenone has many synthetic possibilities. It can be easily reduced to furyl-1-phenyl-3-propanol-3 which has been reacted with phosphorus pentachloride to give the chloride. It is safe to predict that a Grignard reagent can be prepared from the chloride, and from the same compound with the furan ring completely reduced. Furfuralacetophenone has been shown to carry out a variety of useful 1:4 addition reactions with the Grignard reagent, p-thiocresol, p-toluenesulfinic acid, and with guanidine. This type of reaction can no doubt be extended to various other conjugated furan compounds, for example, furfuralacetone.

Furfuralacetone has been reduced to tetrahydrofuryl-1-butanol-3, from which the bromide has been prepared. A very interesting Grignard reagent can be easily prepared in excellent yields (94%) from the bromide. m-Nitrobenzalfurfuralacetone is a stable, yellow, crystalline compound new to the literature. The properties of this compound have not been studied.

5-Nitrofurfuryl acetate has been prepared from furfuryl acetate by nitration in acetic anhydride. 5-Nitrofurfuryl alcohol can be prepared by hydrolysis of the acetate with sulfuric acid. In the past several years some new derivatives of well-known furan compounds have been prepared. These derivatives have not as yet been investigated to the limit of their possibilities. The furfural compounds now obtainable from the Eastman Kodak Company are listed on the last page of this publication.

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Liquids for Molecular Weight Determination by the Freezing Point Method

THERE are three methods in general use for determining the molecular weight of organic substances. These include the Victor Meyer method of measuring the volume of vapor obtained from a known weight of the substance; the elevation of boiling point of a given solvent when a weighed amount of the compound is dissolved in it; and the lowering of the freezing point under the same conditions. The first method is not applicable with substances which vaporize only at high temperatures or which decompose at or near their boiling points. Of the other two procedures, the one using the freezing point depression is usually preferred since the molecular lowering is always numerically greater than the boiling point elevation.

The actual difference between the freezing point of the solvent, with and without the added substance, is determined in the usual Beckmann apparatus. By substituting in the following equation the molecular weight is obtained.

$$M = C \frac{s}{W \times \triangle}, \text{ where}$$

M = Mol. weight of the substance
s = Weight of substance in grams
C = F. P. constant of solvent
W = Weight of solvent in kilograms
$\triangle$ = Observed f. p. depression

Benzene, perhaps, is the solvent most often used for determining the molecular weight of an unknown organic substance. There are, however, a number of other compounds which are used quite often to give better solubility. These include acetic acid, phenol, nitrobenzene and camphor. The first three are hygroscopic and require special apparatus to protect the solutions from moisture. Water with its low molecular weight causes a noticeable freezing point lowering even in minute quantities, and for this reason has to be carefully guarded against.

Dioxan (diethylene dioxide) has been recommended on account of its good solvent properties and its chemical inertness. Cyclohexane has found use in determining the molecular weights of petroleum products. The following table gives the constant C and the approximate freezing point for some of the organic solvents commonly used in molecular weight determinations.

SOLVENT	C	F. P.
Acetic Acid	3.9	16.6
Benzene	5.1	5.5
Benzil	10.5	95.2
Camphor	49.5	174.
Cyclohexane	20.0	6.5
1.4 Dioxan	4.9	11.
Ethylene Bromide	12.5	10.0
Formamide	3.8	3.0
Naphthalene	6.9	80.1
Nitrobenzene	6.9	5.7
Phenanthrene	12.0	99.3
Phenol	7.5	41.
p-Toluidine	5.2	43.5
Tribromophenol	20.4	96.
Urethane	5.1	48.
p-Xylene	4.3	13.

A mixture of two compounds can sometimes be used to advantage as a solvent, the value for C being determined experimentally with solutes of known molecular weight.

Eastman Organic Chemicals as Analytical Reagents

XXI Reagents for Vanadium.

ANILINE

Tananaev and Panchenko, Chem. Abs. *24*, 567 (1930)

To detect vanadium in steels and alloys a very small piece of the metal is dissolved on a watch glass with aqua regia and the hydrochloric acid removed by evaporating with an excess of nitric acid. This prevents other oxidizing anions affecting the reagent. A drop of the metallic solution is then placed on a filter paper which has been moistened with a drop of a solution made by mixing equal parts of aniline and concentrated hydrochloric acid. An intense blue coloration is formed even if the drop contains as little as 0.003 mg. vanadium.

DIPHENYLBENZIDINE

Willard and Young, Ind. & Eng. Chem. *20*, 764 (1928)

The vanadium is oxidized to vanadic acid by potassium bromate which does not affect the chromium salts present. After destroying the excess bromate by boiling, the vanadic acid is titrated with ferrous sulfate, using a 0.1% solution of diphenylbenzidine in concentrated sulfuric acid as an indicator. At the endpoint the color changes from blue to green, and is more pronounced if sodium acetate is added to partly neutralize the acids present. Tungsten interferes with the color formation and must be removed previously.

SAFRANINE

Kolthoff and Furman, Volumetric Analysis, Vol. II (1929) p. 326

The leuco forms of certain dyestuffs, safranine for instance, are changed to their colored forms at the potential which corresponds to the oxidation of bivalent vanadium to its trivalent stage. The vanadium solution is reduced by shaking with lead amalgam; then the indicator is added with additional shaking until it also is reduced. After removing the amalgam, the solution is titrated with copper sulfate to a reddish-violet coloration. Iron does not interfere.

Eastman Organic Chemicals Derived from Furfural

The following furfural derivatives are now included in our list of 3000 Eastman Organic Chemicals. Those in italics are mentioned in the article on page one.

iso-Amyl Furoate
n-Butyl Furoate
Ethyl Furoate
Furacrylic Acid
Furan
Furfural
Furfuralacetone
Furfuralacetophenone
Furfural Diacetate
Furfuraldoxime
Furfuramide
Furfuryl Acetate
Furfuryl Alcohol
Furil
Furoamide
Furoic Acid
Furoin
Furonitrile
Furoyl Chloride
Furylacrolein
Furylacroleinoxime
Furylacrylamide
Furylacryloyl Chloride
Methyl Furoate
m-Nitrobenzalfurfuralacetone
n-Propyl Furoate
Tetrahydrofurfuryl Acetate
Tetrahydrofurfuryl Alcohol
Tetrahydrofurfuryl Propionate

A Reminder

The Fourth
Organic Chemistry Symposium
will be held at New Haven, Conn.
December 28-30, 1931